HYDRODESULFURIZATION OF DIBENZOTHIOPHENE CATALYZED BY SULFIDED CoO-MoO$_3$/γ-Al$_2$O$_3$: THE REACTION KINETICS

D. H. Broderick and B. C. Gates

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

INTRODUCTION

A renewed interest in hydrodesulfurization has come about largely as a result of the need to process more and heavier feedstocks, including synfuels. It has been recognized that model compounds like thiophene are not representative of the least reactive sulfur-containing constituents of these feedstocks. More representative compounds are dibenzothiophenes and benzonaphthothiophenes, which are present in high concentrations in heavy oils (and especially in coal-derived liquids) and are one to two orders of magnitude less reactive than thiophene (1,2).

There is a need for quantitative kinetics characterizing hydroprocessing of these relatively unreactive compounds at temperatures and pressures representative of commercial operation. The goal of this research was to determine detailed kinetics of dibenzothiophene hydrodesulfurization using a high-pressure flow microreactor (3). Earlier work had established the reaction network in dibenzothiophene hydrodesulfurization catalyzed by a commercial presulfided CoO-MoO$_3$/ γ-Al$_2$O$_3$ (4). Early kinetics studies of dibenzothiophene hydrodesulfurization (5,6) fail to account for the complete reaction network and are lacking in experimental detail. Recent kinetics studies (7,8) of dibenzothiophene hydrodesulfurization also fail to provide sufficient detail of the reaction network, and the range of hydrogen partial pressures applied was so low and not all the parameters in the rate equations could be determined from the data.

In the present study rates of the two primary reactions of dibenzothiophene with hydrogen were measured independently, and the full set of data was analyzed and summarized in the form of Langmuir-Hinshelwood rate equations. The data allowed precise estimation of all the kinetics parameters at three temperatures.

EXPERIMENTAL

Materials

The catalyst was a commercial CoO-MoO$_3$/γ-Al$_2$O$_3$ (American Cyanamid HDS 16A) which was crushed and sieved to 149-178 μm (80-100 mesh) particle size and sulfided in situ. Catalyst compositions are given elsewhere (4). Dibenzothiophene (Eastman, reagent grade) was dissolved in n-hexadecane (Humphrey Chemical Co., specially distilled Lots No. 2270375 and 4090577), and the solution was filtered through a 0.5 μm filter element (Milipore). Biphenyl (Eastman, reagent grade) was used as supplied. Hydrogen was obtained from Linde as 3500 psi grade and treated as described below to remove traces of moisture and oxygen. H$_2$S was supplied by Linde in custom mixtures with hydrogen in concentrations of 0.5 to 10 mole% H$_2$S. Alundum "RR" (Fisher

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Scientific, Blue Label) was sieved to 90 mesh and used as an inert reactor packing.

A high-pressure flow microreactor, described in detail by Eliezer et al. (3), was modified to allow for saturation of the feed mixture with a predetermined H_2S partial pressure (9). The catalyst (6.5×10^{-5} to 1.2×10^{-4} kg) was mixed with alundum (2.31×10^{-4} to 4.25×10^{-4} kg) to give the range of bed volumes [$(2.0-3.6) \times 10^{-7}$ m^3] and bed heights [$(2.5-4.5) \times 10^{-2}$ m]. The catalyst was presulfided in the reactor for two hours in a 5.0×10^{-7} to 8×10^{-7} m^3/s flow of 10 vol% hydrogen sulfide in hydrogen at atmospheric pressure and 673°K.

Reactant solutions containing 0.3-4.9 mole% dibenzothiophene in n-hexadecane or 1.24 mole% dibenzothiophene and 0.6 or 2.9 mole% biphenyl in n-hexadecane were prepared. After the solution (5×10^{-4} to 7×10^{-4} m^3) had been loaded into a stirred autoclave, it was saturated with hydrogen or hydrogen plus H_2S at predetermined partial pressures after the mixture had been purged for 2 hr with the gas mixture. H_2S partial pressures were varied from 0 to 1 atm, and hydrogen partial pressures were varied between 34 and 150 atm. Low-pressure gas solubility data served as a basis for extrapolation to high saturation pressures, as described elsewhere (9), for calculating hydrogen and H_2S concentrations in the reactor. Reactant concentrations used to correlate the reaction rate data were calculated for the liquid density at the temperature and pressure of the reactor.

Immediately after sulfiding of the catalyst, the reactor was cooled to 573°K, and flow of reactant mixture was initiated. The pressure in the reactor was maintained at 178 ± 7 atm to ensure against formation of a gas phase inside the reactor. A catalyst break-in period of 50 to 72 hr was allowed, after which the reactor was run with differential conversion of dibenzothiophene to obtain reaction rate data. Over an extended period, hydrogen and H_2S partial pressures were varied, and solutions with the above-mentioned dibenzothiophene concentrations were each investigated at 548, 573 and 598°K. Throughout each run, the rate of reaction was repeatedly measured at the standard condition of 573°K, 96 atm hydrogen partial pressure, 1.24 mole% dibenzothiophene, and 0 or 0.16 atm H_2S partial pressure; these data demonstrated the lack of significant catalyst deactivation.

At each run condition, four to eight liquid product samples were collected and analyzed by glc. An Antek 462 gas chromatograph equipped with a flame ionization detector and an electronic integrator was used. The column was a 3.4 m stainless steel column having a 2.3×10^{-3} m ID and packed with 3% SP-2100 DB (methyl silicone fluid--the basic sites were deactivated) on 100-200 mesh Supelcoport (Supelco) at 423°K with a helium carrier-gas flow rate of about 5×10^{-7} m^3/s. Gaseous products, such as H_2S and any light cracking products, were not collected. In the routine analysis, dibenzothiophene, biphenyl, cyclohexylbenzene, and 1,2,3,4-tetrahydrodibenzothiophene were determined quantitatively. Another product formed in equilibrium with 1,2,3,4-tetrahydrodibenzothiophene, i.e., 1,2,3,4,-10,11-hexahydrodibenzothiophene (4), was masked by the solvent.

Using a wall-coated open tubular column (Perkin-Elmer OV-101) in a Perkin-Elmer 3920 B gas chromatograph, a sufficient number of samples were reanalyzed to establish the equilibrium constant for the reaction [1,2,3,4-tetrahydrodibenzothiophene + H_2 $\rightleftarrows$ 1,2,3,4,10,11-

hexahydrodibenzothiophene] at the three temperatures studied.
Equilibrium constants are given in Table 1. The concentration of
1,2,3,4,10,11-hexahydrodibenzothiophene was then calculated for
each sample from the equilibrium constant and the known concentration
of hydrogen and 1,2,3,4-tetrahydrodibenzothiophene. Total aromatic
carbon in the product stream was typically 98 to 99% of the amount of
dibenzothiophene in the feed mixture.

RESULTS

Preliminary experiments reported earlier (4) showed that the
reactor filled with alundum alone had negligible activity for dibenzo-
thiophene hydrodesulfurization, and intraparticle and extraparticle
mass transfer resistances were negligible.

Addition of 0.02 mole of H_2S/liter of reactant solution was
necessary to stabilize the catalyst (10). With constant catalytic
activity, rates were determined from differential conversions for a
wide range of reactant and product concentrations at 548, 573, and
578°K; detailed data are given elsewhere (9). Concentrations and
temperatures were changed randomly throughout, with periodic activity
checks at the standard conditions.

Data were plotted as fractional conversion to cyclohexylbenzene,
to biphenyl, and to cyclohexylbenzene plus 1,2,3,4-tetrahydrodi-
benzothiophene plus 1,2,3,4,10,11-hexahydrodibenzothiophene (9).
The plots show a linear dependence of conversion on WHSV, and the
first set of data falls near a curve that approaches the origin with
near-zero slope. These results are consistent with the reaction net-
work proposed for dibenzothiophene hydrodesulfurization by Houalla et
al. (4). This network indicates two primary reactions: Hydrogenation of
one aromatic ring gives an equilibrium mixture of 1,2,3,4-tetrahydrodi-
benzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene; hydro-
desulfurization of these two intermediates occurs rapidly to give
cyclohexylbenzene. This combination of reactions is referred to as
the hydrogenation route, and this combination of products determined
rates of hydrogenation of dibenzothiophene. The second reaction was
direct hydrodesulfurization of dibenzothiophene to give biphenyl,
which is referred to as the hydrogenolysis reaction. Biphenyl also
reacted with hydrogen to give cyclohexylbenzene, but this reaction
was typically two orders of magnitude slower than the rate of diben-
zothiophene hydrogenolysis (11).

In summary, the reactant and product concentration data give
the overall rate of dibenzothiophene disappearance and also the rates
of the two primary reactions of dibenzothiophene, one aromatic ring
hydrogenation, and the other hydrogenolysis.

There was a consistent discrepancy in the results indicated by
lack of closure of the mass balance on carbon. The sum of the hydro-
genation and hydrogenolysis rates was on the average 80-85% of the
rate of dibenzothiophene disappearance. The cause of this imbalance
could not be determined, but it appears most likely to have been the
result of some cracking to volatiles lost in sample collection; it is
possible that some heavier products were formed, but the lack of
catalyst deactivation suggests that the former possibility is more
likely. The rate of unobserved product formation was virtually
independent of reaction conditions, and the lack of closure of the

mass balance therefore did not prevent meaningful measurement of the reaction rates.

Representative plots of some of the rate data are given in Figures 1-3. A Langmuir dependence of rate on dibenzothiophene concentration is suggested for each reaction. The rate of hydrogenation is linearly dependent on hydrogen concentration, and the rate of hydrogenolysis shows a Langmuir dependence on hydrogen concentration. Inhibition by hydrogen sulfide was observed for dibenzothiophene hydrogenolysis, but a striking and surprising absence of hydrogen sulfide inhibition is noted for hydrogenation. The effect of biphenyl concentration on the overall rate of dibenzothiophene conversion was negligible at the lower temperatures; a small inhibition effect was observed at 598°K.

DISCUSSION

A number of rate equations, both purely empirical equations and equations corresponding to Langmuir-Hinshelwood models, were evaluated in terms of their ability to represent the data for dibenzothiophene hydrogenation and hydrogenolysis. An independent set of equations was considered for each of the two reactions. The full set of equations is considered elsewhere (9), and here we consider only the equations giving the best fits to the data.

A non-linear least-squares regression analysis was used with each equation in Tables 2 and 3 to determine the best equations for representing the data. A library program, NLLS (1977), from the University of Delaware Computing Center (based on the Marquardt regression technique) was used. The output of the program includes the parameter values giving the best fit as determined by the routine and several statistical measures of the goodness of fit. These are (1) ϕ_{min}, the minimized sum of the squares of the differences between the observed and predicted rates for each condition, (2) a correlation matrix representing the degree of independence of each of the equation parameters from the other parameters, and (3) non-linear 95% confidence limits given as an upper and lower bound on the value of each of the parameters. Summarized in Tables 2 and 3 are the parameter values, the largest difference between the parameter value and the upper or lower bound, and the calculated ϕ_{min} values. The full sets of equations evaluated for each reaction are given in Broderick's thesis (9).

In addition to the statistical criteria of goodness of fit, there are several criteria determining whether an equation has physical meaning: (1) The estimated rate constant and adsorption constants should be positive or include positive values within their error bounds; (2) a plot of the logarithm of the rate constant versus reciprocal absolute temperature (Arrhenius plot) should be linear with a negative slope; (3) a plot of the logarithm of each adsorption equilibrium constant versus reciprocal absolute temperature (van't Hoff plot) should be linear with a positive slope except when chemisorption is endothermic; and (4) a visual comparison between experimentally measured trends and predicted curves should show satisfactory agreement.

The six best equations for the hydrogenolysis reaction data are given in Table 2. Of these, the first four can be derived from the Langmuir-Hinshelwood model assuming various forms of competitive and noncompetitive adsorption, dissociative or undissociative. The last

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two equations are similar in form but do not correspond to any simple Langmuir-Hinshelwood model.

Equations (HS-3), (HS-5), and (HS-6) were found to satisfy all the physical and statistical criteria enumerated above. If, in addition, an equation of Langmuir-Hinshelwood formulation is pre-ferred, Eq. (HS-3) is the only acceptable choice. Eq. (HS-1) gives a poorer fit, judging by the magnitude of ϕ_{min}. Eqs. (HS-2) and (HS-4) showed strong parameter correlation and relatively large deviations from linearity of the Arrhenius plot.

Eq. (HS-5) differs from Eq. (HS-3) only in the half power on the term $K_S C_S$ in the denominator. That same power on $K_S C_S$ in Eq. (HS-6) is largely responsible for the good fit observed for this equation as well. The half power on $K_S C_S$ in Eq. (HS-5) might be interpreted as a suggestion that adsorption of H_2S may occur dissociatively. This suggestion is not unprecedented (12), but it is considered speculative if based only on kinetics data.

Eq. (HS-3) is recommended as the best equation resting on a Langmuir-Hinshelwood model for representing the data for hydrogenoly-sis at all conditions studied. From the Arrhenius plot for this equation, the activation energy, determined from the temperature dependence of $k/K_0 K_S$ is 30 kcal/gmole. Following the Langmuir-Hinshel-wood model, the heats of adsorption for dibenzothiophene, H_2S, and hydrogen were calculated to be -4.5, -5.3, and 8.4 kcal/gmole, respectively. The positive value for the heat of adsorption of hydrogen was observed for all of the equations tested and is perhaps an anomaly associated with the imprecision in the data; the 90% confidence limits on the heat of adsorption are large and include negative values.

Data for the rate of dibenzothiophene hydrogenation were best represented by the equations in Table 3; other equations are con-sidered in Broderick's thesis (9). Differences in goodness of fit among these four equations are relatively small. Eq. (HN-1) is recommended for its goodness of fit, its simple form, and its low parameter correlation and error bounds relative to the other equa-tions. Eqs. (HN-2) and (HN-3) have high error bounds on K_H, and Eqs. (HN-2) and (HN-4) show large deviations from linear Arrhenius plots. Differences in ϕ_{min} are not significant when compared with the standard deviations of the data. The temperature dependence of k' (defined as k/K_D) and K_D were calculated from Arrhenius and van't Hoff plots. An activation energy of 27.6 kcal/gmole and a heat of adsorp-tion for dibenzothiophene of -1.4 kcal/gmole resulted.

The literature on hydrogenolysis reaction kinetics in hydrode-sulfurization of thiophenic compounds catalyzed by Co-Mo/γ-Al$_2$O$_3$ is in general agreement with the results for dibenzothiophene. Much of the work has concerned thiophene (13-16) and benzothiophene (17) at pressures near atmospheric and for narrow ranges of hydrogen partial pressure. There is much evidence that the principal reaction for both compounds is hydrogenolysis. There is strong agreement that the dependence of rate on the concentrations of thiophenic reactant and of H_2S is the same as shown in Eq. (HS-3). The dependence of rate on hydrogen partial pressure has typically been represented as first order at low partial pressures (13-14,16), although data have been meager. One of the contributions of the present kinetics study was

therefore the clear determination of the dependence of rate on hydrogen concentration under conditions more typical of commercial processes.

The results of previous kinetics studies of dibenzothiophene differ somewhat from the kinetics for hydrogenolysis reported here. For conditions similar to those applied here but for a maximum hydrogen partial pressure of 31 atm, Espino et al. (7) and Mahoney et al.(8) reported a rate equation with a power of 1 on the denominator term for adsorption of H_2S and dibenzothiophene. Mahoney et al. observed a first order dependence of rate on hydrogen partial pressure. In neither study was the rate of hydrogenation distinguished from the rate of hydrogenolysis, and we infer that under the reported reaction conditions, both reactions contributed to the measured rates of dibenzothiophene conversion. Thus the reported kinetics do not represent hydrogenolysis alone, but correlate all reaction rates. They are in good agreement with the sum of the equations for hydrogenolysis and hydrogenation determined in this work (9).

Reported activation energies for hydrogenolysis of thiophene and benzothiophene range from 4 to 20 kcal/gmole (9) compared with approximately 30 kcal/gmole for the less reactive dibenzothiophene. If we interpret the Langmuir-Hinshelwood rate equation literally (which is surely an oversimplification), we can infer values of the heats of adsorption from the slopes of the van't Hoff plots. The heat of adsorption calculated for H_2S implied by the hydrogenolysis rate equation falls within the range reported in the literature (5-20 kcal/gmole), and the value for dibenzothiophene (4.5 kcal/gmole) is lower than those for thiophene and benzothiophene (12-24 kcal/gmole).

Literature on the hydrogenation reaction of dibenzothiophene consists of the work by Houalla et al. (4) and Bhinde (18), who used large excesses of hydrogen and accurately approximated the rate of dibenzothiophene disappearance by hydrogenation as a pseudo first-order reaction. Hydrogenations of other heteroaromatics, such as quinoline and pyridine, and of aromatics such as biphenyl, naphthalene, and benzene catalyzed by presulfided Co-Mo/γ-Al_2O_3 have been studied, and limited kinetics data have been reported. For biphenyl, Espino et al. (7) represented rate data with a Langmuir-Hinshelwood equation indicating competitive adsorption of biphenyl and cyclohexylbenzene on one kind of site and of hydrogen on another. No measure of inhibition by H_2S was determined. Few details were given concerning the data and the criteria for selection of the rate equation. For pyridine (19) and quinoline (18,20) the rate of hydrogenation of the aromatic ring (or rings) was approximated as first order in heteroaromatic, but the rate constant decreased with increasing reactant concentration, suggesting self inhibition of reaction. The order of reaction in hydrogen partial pressure ranged from 1 to 1.5 for pyridine, and from 0.5 to 1 for quinoline. The effect of H_2S on the rate of hydrogenation of quinoline was negligible, and for pyridine, H_2S was an inhibitor when <2 mole% H_2S was present, and otherwise the rate was independent of H_2S concentration. For the most part, these kinetics results for hydrogenation reactions of nitrogen-containing aromatics are in agreement with the dibenzothiophene hydrogenation kinetics represented by Eq. (HN-1). These results suggest a rather wide application of Eq. (HN-1) for hydrogenation of aromatics and heteroaromatics.

Studying the hydrodesulfurization kinetics of dibenzothiophene has provided a unique opportunity to examine carbon-sulfur bond hydrogenolysis reactions and aromatic ring hydrogenation under identical conditions. Both reactions are of major importance in hydroprocessing. The kinetics results provide some insight into the mechanisms of the catalytic mechanisms, on one hand, and suggestions for tailoring the catalyst and process conditions to the desired product selectivity, on the other.

Comparison of Figures 1 and 2 and Eqs. (HS-3) and (HN-1) suggests that for sulfided $CoO-Mo/\gamma-Al_2O_3$ catalyst, the reaction mechanism and catalytic sites differ for hydrogenation and hydrogenolysis. The literature supports the proposal of two different kinds of sites for hydrogenation and hydrogenolysis. The evidence is provided by results of poisoning (14,21,22) and kinetics (13,14,17,18) studies. One kind of site is strongly poisoned by bases such as pyridine and quinoline, and the other is less acidic and less sensitive to such poisons. The former sites are associated with hydrogenation activity and the latter with C-S bond scission activity, although some overlap is expected. From Equation (HN-1), it is inferred that the hydrogenation sites do not bond strongly to hydrogen or H_2S, but they do bond strongly to dibenzothiophene. In contrast, H_2S does compete strongly with dibenzothiophene for hydrogenolysis sites, as follows from Eq. (HS-3). The form of this equation suggests the hydrogen adsorbs on still another type of site, as is expected from the known formation of -SH groups on the surface.

The structure of dibenzothiophene adsorbed on the catalyst surface is unknown, but the extensive hydrogenation of the benzenoid rings suggests considerable ring interaction with the surface. Dibenzothiophene, being a planar molecule, is believed to adsorb in a plane parallel to the catalyst surface favorable to metal-ring interactions at anion vacancies on the surface. Proposals for adsorption via π-complex formation (23,24) or multi-point bonding (25) are strengthened by these results.

A well-recognized concern in hydroprocessing is the consumption of expensive hydrogen. Considering quantitatively the marked differences in the kinetics reported here for hydrogenation and hydrogenolysis of dibenzothiophene, we recognize two important processing variables for minimizing the hydrogen consumption in hydrodesulfurization. Decreased H_2S concentrations (obtainable by recycle gas scrubbing) favor hydrogenolysis. The change in selectivity is dramatic for H_2S concentrations between about zero and 0.1 gmole/liter. Temperature also strongly influences the relative rates of hydrogenation and hydrogenolysis. As the temperature is raised, the relative rate of hydrogenolysis increases sharply. The selectivity for dibenzothiophene hydrogenolysis also increases with increasing concentration of quinoline, an inhibitor of both hydrogenation and hydrogenolysis reactions (18). It is important to remember that, in general, competition between the sulfur-containing reactant and other feed components may alter the kinetics and selectivity. Recognizing this limitation, we recommend the kinetics presented here for qualitative guidance in process design and suggest that the form of the rate equation (modified to account for the presence of various inhibitors) could be of use in reaction engineering models for process simulation.

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NOMENCLATURE

C_i Concentration of Species "i"
D Dibenzothiophene
H Hydrogen (H_2)
HHD Hexadydrodibenzothiophene
k Observed Rate Constant

k' Intrinsic Rate Constant $(= k/K_D/K_H)$
K_i Adsorption Equilibrium Constant of Species i
S Hydrogen Sulfide (H_2S)
THD Tetrahydrodibenzothiophene

TABLE 1

Temperature Dependence of the
Equilibrium Constant K_X

Temp., $^\circ K$	$K_X{}^a$
548	5.76 ± 0.29^b
573	3.45 ± 0.33
598	2.05 ± 0.17

$K_X \simeq EXP\ (-\Delta G^\circ/RT)$,

$\Delta G^\circ = 13,400 - T(^\circ K) \times 10.55$ cal/gmole

[a] K_X is defined as $X_{HHD}/X_H X_{THD}$ where X_i is the mole fraction of species i.

[b] K_X was calculated for various X_H and averaged. Error bound is standard deviation.

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TABLE 2

Rate Equations Best Fitting Dibenzothiophene Hydrogenolysis Kinetic Data

Rate Equation	Temp., °C	$10^6 \times k^a$ liter²/(gmole·g of catalyst·sec)	K_D, liter/gmole	k_H, liter/gmole	K_S, liter/gmole	$10^{16} \times \phi_{min}$, (gmole / g of catalyst·sec)²
(HS-1) $\dfrac{k\,C_D C_H}{(1+K_D C_H + K_S C_S)^2}$	275	11.4 ± 1.3	10.3 ± 3.0	--	86 ± 16	0.366
	300	39.9 ± 4.3	7.2 ± 2.5	--	74 ± 12	6.81
	325	130 ± 15	6.8 ± 2.6	--	59 ± 11	82.3
(HS-2) $\dfrac{k\,C_D C_H}{(1+K_D C_D + K_S C_S + K_H C_H)^2}$	275	30.1 ± 3.9	18.1 ± 5.8	2.9 ± 1.3	137 ± 31	0.342
	300	200 ± 22	18.5 ± 6.1	6.0 ± 1.4	161 ± 27	5.39
	325	439 ± 53	14.5 ± 5.0	4.1 ± 1.2	103 ± 21	63.3
(HS-3) $\dfrac{k\,C_D C_H}{(1+K_D C_D + K_S C_S)^2 (1+K_H C_H)}$	275	15.7 ± 2.0	11.5 ± 3.5	1.6 ± 1.0	86 ± 19	0.341
	300	69.3 ± 7.5	8.7 ± 2.7	3.2 ± 1.1	75 ± 12	5.36
	325	215 ± 26	8.2 ± 2.8	2.9 ± 1.2	58 ± 12	61.4
(HS-4) $\dfrac{k\,C_D C_H}{(1+K_D C_D + K_S C_S)^2 [1+(K_H C_H)^{1/2}]^2}$	275	20.3	11.4	0.46	86.5	0.341
	300	106.3	8.5	1.72	74.9	5.41
	325	315	8.1	1.40	58.1	64.6
(HS-5) $\dfrac{k\,C_D C_H}{[1+K_D C_D + (K_S C_S)^{1/2}]^2 (1+K_H C_H)}$	275	59.9 ± 4.7	23.9 ± 3.8	1.77 ± 0.59	868 ± 144	0.122
	300	205 ± 14	16.4 ± 2.7	3.20 ± 0.61	518 ± 72	1.99
	325	503 ± 33	13.3 ± 2.2	2.96 ± 0.60	256 ± 38	18.7
(HS-6) $\dfrac{k\,C_D C_H}{(1+K_D C_D + K_H C_H)^2 [1+(K_S C_S)^{1/2}]}$	275	25.1 ± 1.9	5.2 ± 1.2	0.89 ± 0.28	270 ± 42	0.122
	300	111.0 ± 7.4	4.7 ± 1.0	1.44 ± 0.27	221 ± 29	1.98
	325	323 ± 21	5.0 ± 0.9	1.38 ± 0.27	127 ± 17	18.3

TABLE 3

Rate Equations Best Fitting Dibenzothiophene Hydrogenation Kinetics Data

Rate Equation	Temp., °C	$10^6 \times k$, $\dfrac{\text{liter}^2}{\text{gmole·g of catalyst·sec}}$	K_D, $\dfrac{\text{liter}}{\text{gmole}}$	K_H, $\dfrac{\text{liter}}{\text{gmole}}$	K_S, $\dfrac{\text{liter}}{\text{gmole}}$	$10^{17} \times \phi_{min}$, $\left(\dfrac{\text{gmole}}{\text{g of catalyst·sec}}\right)^2$
(HN-1) $\dfrac{k\,C_D\,C_H}{(1+K_D C_D)^2}$	275	2.78 ± 0.11	7.39 ± 0.89	--	--	1.30
	300	8.11 ± 0.24	7.70 ± 0.72	--	--	7.14
	325	20.9 ± 0.57	6.61 ± 0.55	--	--	24.3
(HN-2) $\dfrac{k\,C_D\,C_H}{(1+K_D C_D)(1+K_H C_H)}$	275	2.95 ± 0.14	7.6 ± 1.07	0.25 ± 0.25	--	1.26
	300	8.60 ± 0.30	7.92 ± 0.85	0.26 ± 0.19	--	6.78
	325	21.6 ± 0.7	6.73 ± 0.67	0.14 ± 0.16	--	23.7
(HN-3) $\dfrac{k\,C_D\,C_H}{(1+K_D C_D + K_H C_H)}$	275	2.98 ± 0.14	8.0 ± 1.1	0.31 ± 0.35	--	1.26
	300	8.69 ± 0.30	8.4 ± 0.9	0.32 ± 0.26	--	6.80
	325	21.7 ± 0.66	6.9 ± 0.7	0.16 ± 0.22	--	23.7
(HN-4) $\dfrac{k\,C_D\,C_H}{[1+(K_D C_D)^{\frac{1}{2}}]^2 (1+K_H C_H)}$	275	4.34 ± 0.18	3.78 ± 0.50	0.27 ± 0.22	--	0.987
	300	12.6 ± 0.4	3.91 ± 0.41	0.27 ± 0.17	--	5.73
	325	30.2 ± 0.74	2.81 ± 0.25	0.16 ± 0.13	--	16.0

FIGURE 1

REACTION RATES IN DIBENZOTHIOPHENE
HYDRODESULFURIZATION AS A FUNCTION OF
HYDROGEN CONCENTRATION AT 300°C

Curves are Predicted by Fitted Rate
Equations Described in the Text

- ● Dibenzothiophene Disappearance
- ■ Hydrogenation
- ▲ Hydrogenolysis

10^9 x Rate, g Mole/g of Catalyst Sec.
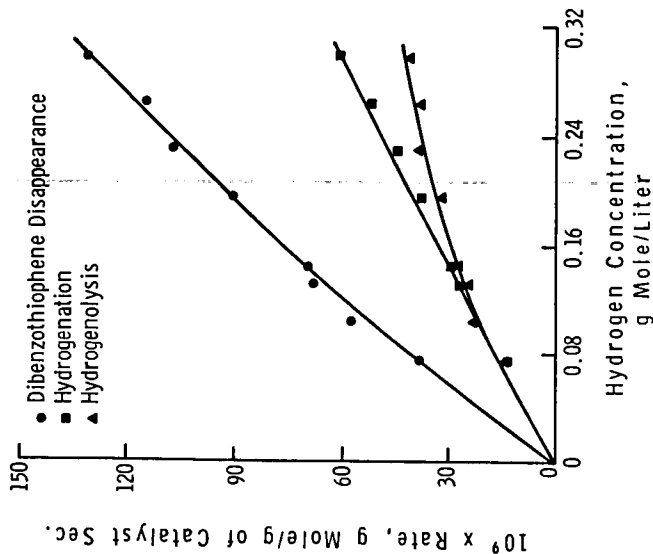
Hydrogen Concentration,
g Mole/Liter

FIGURE 2

REACTION RATES IN DIBENZOTHIOPHENE
HYDRODESULFURIZATION AS A FUNCTION OF
DIBENZOTHIOPHENE CONCENTRATION AT 300°C

Curves are Predicted by Fitted Rate
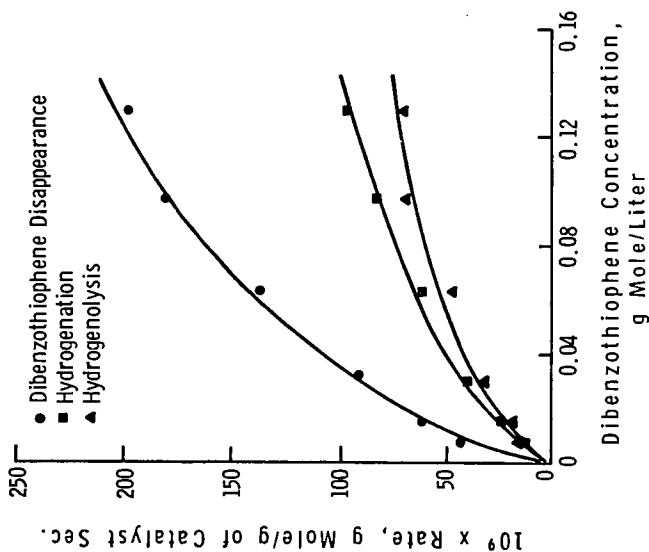Equations Described in the Text

- ● Dibenzothiophene Disappearance
- ■ Hydrogenation
- ▲ Hydrogenolysis

10^9 x Rate, g Mole/g of Catalyst Sec.

Dibenzothiophene Concentration,
g Mole/Liter

FIGURE 3

REACTION RATES IN DIBENZOTHIOPHENE HYDRODESULFURIZATION AS A FUNCTION OF HYDROGEN SULFIDE CONCENTRATION AT 300°C

Curves are Predicted by the Fitted Rate Equations Described in the Text